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The photoelectrochemical properties of n-GaAs and n-Si are compared in nonaqueous electrolytes. Si is the more sensitive material to surface treatment, and is more prone to anodic passivation. Surface adsorption of Ru or basic heterocyclic polymers greatly improves photocurrent yields for both materials, possibly due to a complexation of surface states.

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(6) NONAQUEOUS ELECTROCHEMICAL PHOTOVOLTAIC CELLS BASED ON n-GaAs AND n-Si

by

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NONAQUEOUS ELECTROCHEMICAL PHOTOVOLTAIC CELLS BASED ON n-GaAs AND n-Si

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Photoelectrochemical devices hold great promise as simple converters of solar energy to electricity or fuels. The efficiency of such conversion hinges on the efficiency of charge separation at the semiconductor/electrolyte interface and on the maximum photovoltages which can be generated. Bard, Wrighton and co-workers (1) have stressed the importance of interface effects in determining photoelectrochemical properties. In this paper we compare the general properties of n-GaAs and n-Si photoelectrodes in nonaqueous electrolytes, and emphasize their relative sensitivity to surface preparation.

The photoelectrochemical behavior of n-GaAs has been investigated in several nonaqueous solvents, including propylene carbonate, acetonitrile, dimethylformamide, methyl formate and methanol. Some rectifying behavior was always observed for crystals of donor density $<10^{18}$ cm^{-3}, even for polished but unetched surfaces. Anodic current in the dark was not observed for redox couples lying well within the band gap, e.g., ferrocene, I^-, tetramethylphenylenediamine. Photovoltages, onsets of photocurrent (i_p) and the shape of the i_p-V curves were dependent on surface preparation. However, when the most reproducible etching treatment was employed, viz., 1:1 H_2O_2:H_2SO_4 "matte" etch, the onset of photocurrent in propylene carbonate appeared at -0.2 to -0.3V vs. SCE independent of redox couple within a range of V(redox) from +0.6 to -0.1V vs. SCE. Hence, under these conditions, the Fermi level of the n-GaAs does not appear to be totally pinned by surface states, and the degree of band bending is sensitive to V(redox) as is the open circuit saturation photovoltage.

In many respects, the behavior of n-Si sharply contrasts that of n-GaAs. Surface abrasion or "fast" etchants such as concentrated HF usually result in metallic, weakly photoresponse electrodes. Best results are achieved by deep polishing of the n-Si followed by treatment with a moderate etchant, such as conc. HF(9), HNO_3(22), H_2O(19). Unlike GaAs, the oxidation products of Si are highly passivating, even those formed on anodization in nonaqueous electrolytes containing <10 ppm H_2O (2). Thus, photocurrents degrade with time unless the electron transfer reaction is fast and highly favored thermodynamically.

In Figure 1, the dark and photoelectrochemistry of n-Si and n-GaAs are compared in PC, 0.5M $LiClO_4$ containing 5 x 10^{-3}M ferrocene (V° = 3.21V vs. Li^+/Li) and 5 x 10^{-3}M nickelocene (V° = 2.87V vs. Li^+/Li). For n-GaAs, no anodic dark current is observed, while the Nc^+/Nc is nearly reversible on Si (V_{fb} = 2.6V). Irradiation of the electrodes with 6328Å light produces anodic photocurrent in both cases. The n-Si displays two separate peaks which were determined to result from photocurrent onsets at separated potentials. Reduction of anodically generated Fc^+

and Nc^+ occurs at potentials positive of the onset of photoanodic current, indicating a sensitivity of the interfacial band energies to the local environment. Conversely, for n-GaAs, only a single photoanodic wave is observed, and cathodic current occurs only cathodic of the photocurrent onset. The behavior of n-Si is consistent with the model of Fermi level pinning put forth by Bard, Wrighton and co-workers (1), while more "classical" behavior is apparent for n-GaAs.

Although the photoelectrochemistry of n-GaAs appears to be less sensitive to surface defects than that of n-Si, positive effects of surface treatment and surface adsorbants are noted for both electrodes. In Figure 2, the outputs of a photoelectrochemical half cell are shown for n-Si in acetonitrile, 1.0M I^-, 0.01M I_2. The positive effect on aqueous n-GaAs/Se^{2-}/Se_2^{-2} cells of Ru(III), reported by the Bell Laboratories group (3), has been shown to occur for n-GaAs in nonaqueous systems in our laboratory. As shown in Figure 2, the same treatment also increases photocurrent yields for n-Si. Interestingly, we have noted similar effects on both electrodes of adsorbed heterocyclic polymer films such as polyvinylpyrrolidone, also indicated for n-Si in Figure 2. Ru(III) on the n-GaAs surface has been shown to decrease the surface recombination velocity of photogenerated minority carriers (3), possibly via redistribution of surface state energies. Such a mechanism of enhanced charge separation may hold for n-Si and the adsorbed polymers as well.

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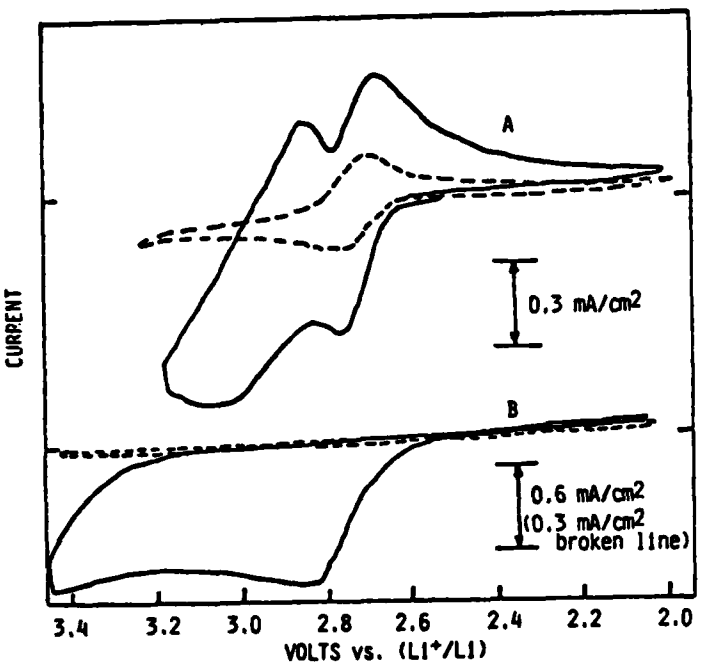

Fig. 1. Cyclic voltammograms in the dark (broken line) and light (6328Å, 15 mW/cm2) of 5 x 10-3M ferrocene and nickelocene in propylene carbonate, 0.5M $LiClO_4$ on A, N-Si([111], 14 Ω-cm) and B, n-GaAs ([100], 0.1 Ω-cm).

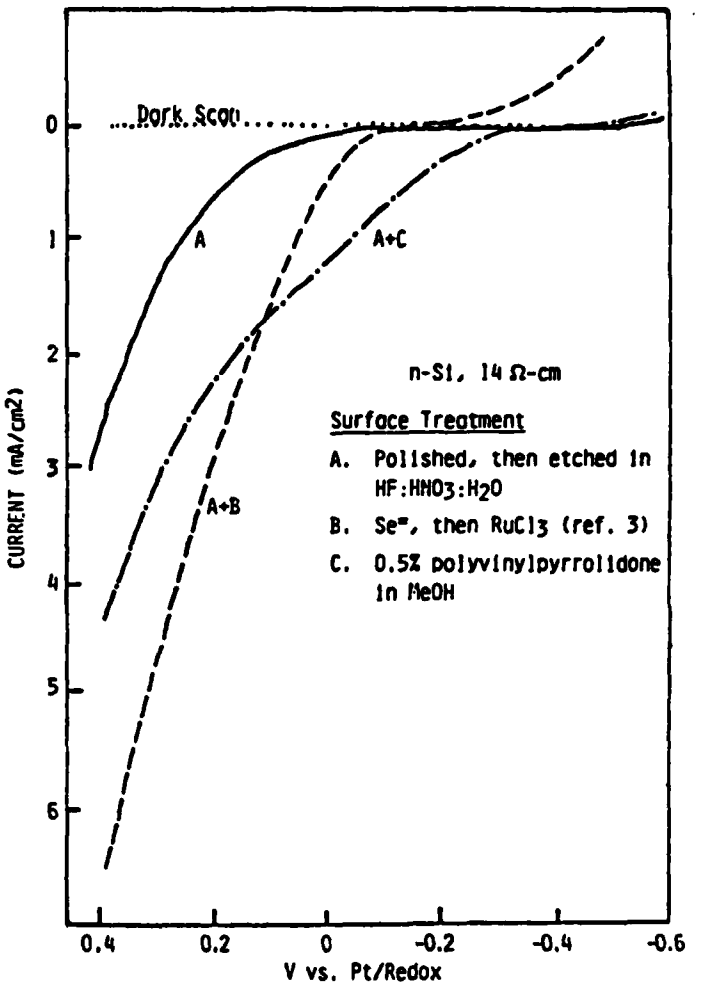

Fig. 2. Current-voltage curves for n-Si in acetonitrile, 1.0M tetrabutylammonium iodide, 0.01M I_2. Irradiation, Xe arc source at 80 mW/cm2.

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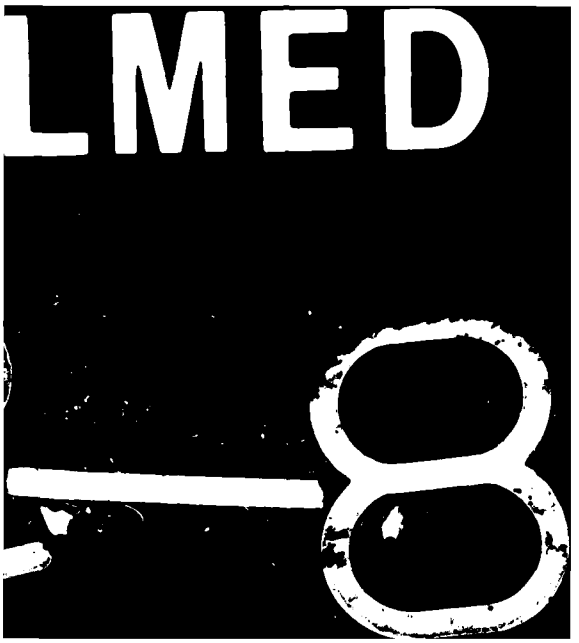
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